Data Evaluation Report of Photodegradation on Soil

PMRA Submission Number {.....}

EPA MRID Number 42899601

Data Requirement: PMRA Data Code: N/A
EPA DP Barcode: N/A
OECD Data Point: N/A
EPA Guideline: N/A

Test material:
Common name:
Chemical name
IUPAC: R-2-(2,4-dichlorophenoxy)propionic acid
CAS name: (2*R*)-2-(2,4-dichlorophenoxy)propanoic acid
CAS No:
Synonyms: N/A

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Signature: James Hetrick
Date: 10-30-10

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Date: 10.6

Company Code:
Active Code:
Use Site Category:
EPA PC Code: 031402

CITATION:

Saxena, Adesh M., S.M. Schweitzer, L. Pena-Cordova, and J. Marengo. 1993. Photodegradation of [^{14}C]-2,4-DP-p Acid in a Sandy Loam Soil Under Artificial Sunlight Irradiation. Performed by Battelle Memorial Institute, Columbus, OH. Submitted by 2,4-DP(1988) Task Force, BASF, Aktiengesellschaft, Germany. MRID 42899601.

Data Evaluation Report of Photodegradation on Soil

PMRA Submission Number {.....} EPA MRID Number 42899601

EXECUTIVE SUMMARY:

The study provides acceptable data on photodegradation of 2,4-DP-p acid on soil. No additional data are needed at this time.

Radiolabeled 2,4-DP-p acid, at 3.2 µg/g, had a photodegradation in soil half-life of 7.6 days (R^2=0.913; k=-0.092 $days^{-1}$). The half-life of 2,4-DP-p acid in the dark control was 20 days (R^2=0.919;k=-0.035 $days^{-1}$). EFED calculated a corrected photodegradation on soil half-life because there was degradation in the dark control. The corrected photodegradation on soil half-life of 2,4-DP-p acid is 12.15 days (k=-0.057 $days^{-1}$). The major photodegradation product was 2,4-dichlorophenol (26.5% of applied at 8 days post treatment). An unidentified degradate also was detected at 4.1 % of applied (0.13 µg/g) at 10 days post treatment. Unidentified radiolabeled residues were also detected in NaOH/polyurethane gas traps (6.3% of applied at 10 days post treatment) and non-labile soil organic matter (< 35% of applied).

MATERIALS AND METHODS:

Arkport sandy loam soil was collected from a site near Waterloo, NY. Physicochemical properties of the test soil are shown in Table 1. Moist test soil was passed through a 2 mm sieve and stored at 4^{O}C.

Preliminary Study

Subsamples of test soil were amended with isotopically diluted radiolabeled 2,4-DP-p acid (isotopic dilution ratio 1:1; ring-labeled; radiopurity= >99.2%; SA= 59.63 µCi/mg) to yield a nominal soil concentration of 3 µg/g. Each soil sample was irradiated with an artificial light source. [**Reviewer Note**: The registrant did not indicate the artificial light source.] Irradiated and dark control samples were incubated at temperature range of 24.3 to 24.9°C. Volatile radioactivity was trapped in sequential gas traps of ethylene glycol, NaOH, and charcoal.

Definitive Study

A subsample of test soil (5 g) was placed into each of twenty-six stainless steel dishes. Each soil sample was amended with radiolabeled 2,4-DP-p acid (isotopic dilution ratio 1:1; ring-labeled; radiopurity= >99.2%; SA= 59.63 µCi/mg) to yield a soil concentration of 3.2 µg/g. Twelve of the samples were used as dark control samples. These samples were placed into an aluminum test container which was connected to sequential gas traps of ethylene glycol and NaOH. Twelve of the samples were placed into a stainless steel vessel equipped with a quartz glass cover. This incubation vessel was connected to sequential gas traps of polyurethane plug, NaOH, and charcoal. Each incubation vessel was continuously flushed with humidified, $C0_2$-free air.

The irradiated samples were exposed to Xenon light (>290 nm) at 12 hour photoperiods. The spectral distribution of the Xenon light is shown Figure 3. Irradiated and dark control soil samples were maintained at a moisture content of 75% field capacity and a temperature range of 24.2 to 24.7^{O}C. Duplicate soil samples were taken immediately post treatment and at 3, 6, 8, 10, 13, and 15 days after irradiation.

Analytical

Each soil sample was extracted with methanol:aqueous H_3PO_4 (90:10 v:v). The soil extracts were filtered and spiked with 0.5M ammonium acetate. The extracted soil was further extracted with 0.5 N NaOH to characterize bound residues to soil.

Soluble residues were separated by HPLC with Sperisorb, S50DS column and a reverse phase solvent system of 0.1% trifluoroacetic acid (TFA) and 0.1% TFA in acetonitrile; separated residues were detected using a radioactivity detector. Soluble residues in selected irradiated samples were also separated by HPLC using a Whitman Partisil column and a normal phase solvent system of toluene: acetic acid 100:1 (v:v) and toluene :isooctane 4:1 (v:v); and separated residues were detected using a radioactivity detector. Soluble residues were also separated by 1-D TLC with acetonitrile: water: ammonium hydroxide 80:18:2 (v:v:v) solvent. The ^{14}C content in soil and gas traps was determined by LSC. The ^{14}C content of extracted soil was determined by combustion-LSC.

RESULTS AND DISCUSSION:

A. Material balance of radioactivity in irradiated and dark control soil samples ranged from 88.1 to 107% of applied radioactive 2,4-DP-p acid (Table II).

B. The half-life of ^{14}C-2,4-DP-p acid in irradiated soil was 7.6 days (R^2=0. 913 ; k=-0.092 days-^{1}) (Table VII; Figure 12). The degradation half-life of 2,4-DP-p in dark control samples was 20 days (R^2=0.919; k=-0.035 days-^{1}) (Table VIII; Figure 13). **Reviewer Note**: A corrected photodegradation half-life of 2,4-DP-p acid was calculated because 2,4- DP-p acid degradation was observed in dark control samples. The corrected photo-degradation in soil half-life for 2,4-DP-p acid is 12.16 days (k=0.057 days-^{1}).]

C. Two degradation products were detected in irradiated and dark control samples (Figures 10 and 11, Table IV). These degradation products had HPLC retention times of 18.2 minutes (Peak 1) and 30 minutes (Peak 2). Peak 1 was co-chromatographed with dichlorophenol (R_t =17.4 minutes) (Figure 14-16). This identification was confirmed using normal phase HPLC and TLC. Peak 2, however, was not co-chromatographed with any known standards. Volatile radioactivity in NaOH gas traps (6.3% of applied at 10 days post treatment) was assumed to be ^{14}C-CO_2. Volatile radioactivity in polyurethane plugs (<0.5% of applied) was not identified. The unidentified volatile residue was assumed to be 2,4-dichlorophenol because it was volatile during preparation of analytical samples.

D. The maximum concentration of 2,4-dichlorophenol in irradiated samples was 26.5% of applied (0.87 µg/g) at 8 days post-treatment and then declined to 15.6% of applied (0.47 µg/g) at 10 days post-treatment (Table V). The degradation product 2,4-dichlorophenol was detected (0.9% applied (0.03 µg/g) in a single dark control sample. The maximum concentration of residue in Peak 2 was 4.1 % of applied (0.13 µg/g) at 10 days post-treatment in the irradiated and dark control samples.

E. Bound residues in soil organic matter (fulvic and humic acids) were detected in irradiated and dark control soil samples (Table IX). Radiolabeled residues were detected in humic acid fraction (19 to 21% of applied), fulvic acid fraction (7.7 to 8.9% of applied), and humin fraction (5.9 to 6.0% of applied).

REVIEW COMMENTS:

A. The registrant did not provide a corrected a photodegradation on soil half-life for 2,4-DP-p acid. EFED believes a corrected photodegradation half-life of 2,4-DP-p acid is needed because 2,4-DP-p degradation was observed in the dark control. The corrected photodegradation in soil half-life for 2,4-DP-p acid is 12.16 days (k=- 0.057 days-^{1}). In future studies, the registrant should correct half-life estimates for any degradation in dark control samples.

Deionized water, Millipore Model Milli RO4 Reverse Osmosis System

Ethylene Glycol, Baker chemicals

Sodium Hydroxide, Baker chemicals

All chemicals were analytical grade or better.

3.4 Test System

The soil used for this study was an Arkport sandy loam soil collected near Waterloo, Seneca County, New York State. The soil and soil characteristics (except bulk density which was determined by Battelle) were provided by the Sponsor. The soil was characterized by EPL-Bioanalytical Services and was the same soil as that used in the aerobic soil metabolism study. The soil was sieved through a 2 mm sieve. The soil was stored at approximately 4°C. The moisture content of the soil as received at Battelle, was 2.9%. Prior to estimating the microbial population, the soil was moistened and incubated at room temperature for seven days. Microbial analysis of the soil was conducted by plating soil dilutions on nutrient agar plates prior to the initiation of the study. After incubation, the microbial population of the soil was determined to be 8.1×10^6 colonies per gram dry weight soil. The physical and chemical characteristics of the soil include:

pH	6.5
Bulk Density	1.31 g/cc
Organic Matter	2.7%
Field Moisture Capacity at 0.33 bar	19.56%
Textural Class	Sandy Loam
Sand	54.5%
Silt	28.9%
Clay	16.6%
Cation Exchange Capacity	9 meq/100g

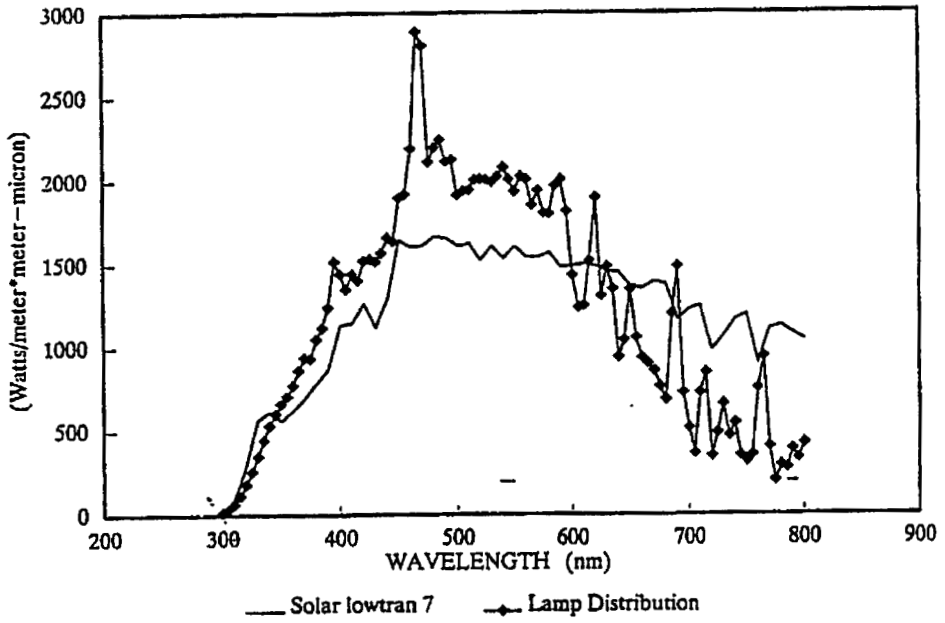


FIGURE 3. **Spectral Distribution of the Xenon Lamp with Comparison to a Solar Spectral Distribution.**

TABLE II. RECOVERY OF APPLIED RADIOACTIVITY, INDIVIDUAL VALUES[a]

Day	Sample[b]	Soil Extracts	Soil-Bound	Volatile Traps[c]	Total
Irradiated Samples					
0	LD-0-A	105.5	1.5	NA	107.0
	LD-0-B	105.2	1.6	NA	106.8
3	L-1-A	87.8	8.5	1.3,(0.1)	97.7
	L-1-B	88.8	8.5	1.3,(0.1)	98.7
6	L-2-A	66.4	20.2	3.2,(0.2)	90.0
	L-2-B	82.2	12.8	3.2,(0.2)	98.4
8	L-3-A	76.2	17.2	4.9,(0.3)	98.5
	L-3-B	61.7	21.0	4.9,(0.3)	87.9
10	L-4-A	65.3	16.3	6.3,(0.5)	88.4
	L-4-B	61.8	19.5	6.3,(0.5)	88.1
Dark Controls					
0	LD-0-A	105.5	1.5	NA	107.0
	LD-0-B	105.2	1.6	NA	106.8
3	D-1-A	96.1	6.6	0.3	103.0
	D-1-B	90.4	6.3	0.3	97.0
6	D-2-A	88.3	7.9	1.1	97.3
	D-2-B	91.1	7.2	1.1	99.4
8	D-3-A	79.6	10.5	2.1	92.2
	D-3-B	80.0	8.4	2.1	90.5
10	D-4-A	79.8	10.8	3.5	94.1
	D-4-B	80.5	10.9	3.5	94.9

[a] All values are expressed as a percentage of radioactivity applied to sample.
[b] Day 0 samples were not irradiated and data from these samples are common to Irradiated and Dark Controls.
[c] For the irradiated samples only, values shown outside brackets are for NaOH traps, and in brackets for the foam plugs. No significant radioactivity was detected in charcoal traps. Only NaOH traps were used for the dark controls.
NA Not applicable.

TABLE VII. HALF LIFE DATA, IRRADIATED SAMPLES

		2,4-DP-p acid	
Day	**Sample**	**Percent of Applied**	**Ln [a]**
0	LD-0-A	105.5	4.66
	LD-0-B	105.2	4.66
3	L-1-A	81.2	4.40
	L-1-B	68.9	4.23
6	L-2-A	53.1	3.97
	L-2-B	55.1	4.01
8	L-3-A	47.8	3.87
	L-3-B	39.5	3.68
10	L-4-A	47.7	3.87
	L-4-B	42.4	3.75

Regression Data	
Constant (y-intercept)	4.60
R squared	0.913
X Coefficient(s) (Slope)	- 0.092
Half-Life	7.6 days

[a] The natural log of percent of applied radioactivity from data in Table V was calculated and plotted versus time.

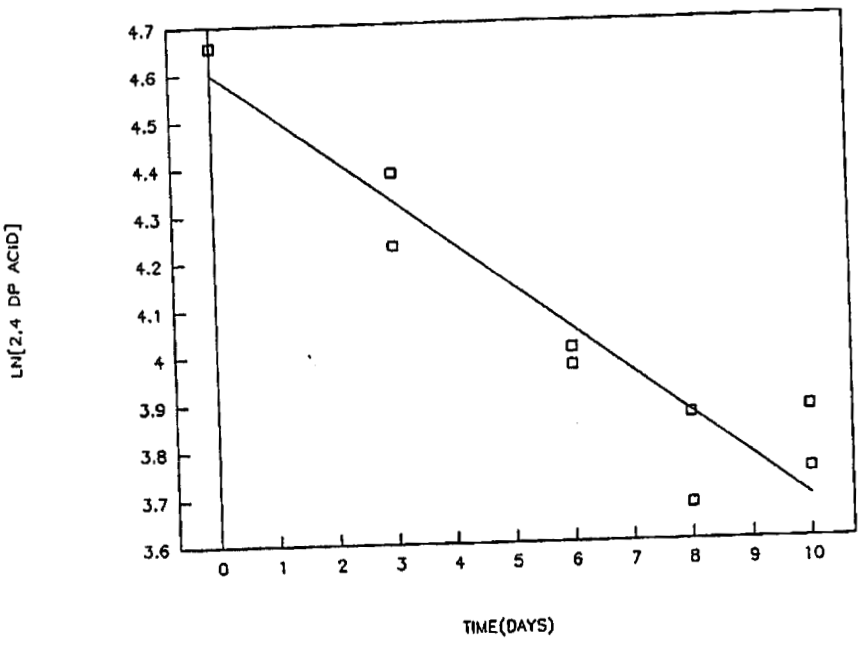


FIGURE 12. **Linear Regression Plot for Half-Life Determination Under Irradiated Conditions. The Half-Life Was 7.6 Days.**

TABLE VIII. HALF LIFE DATA, DARK CONTROL SAMPLES

		2,4-DP-p acid	
Day	Sample	Percent of Applied	Ln[a]
0	LD-0-A	105.5	4.66
	LD-0-B	105.2	4.66
3	D-1-A	95.5	4.56
	D-1-B	89.7	4.50
6	D-2-A	84.9	4.44
	D-2-B	89.1	4.49
8	D-3-A	74.9	4.32
	D-3-B	74.6	4.31
10	D-4-A	75.7	4.33
	D-4-B	76.4	4.34

Regression Data	
Constant (y-intercept)	4.65
R squared	0.919
X Coefficient(s) (Slope)	- 0.035
Half-Life	20 days

[a] The natural log of percent of applied radioactivity from data in Table V was calculated and plotted versus time.

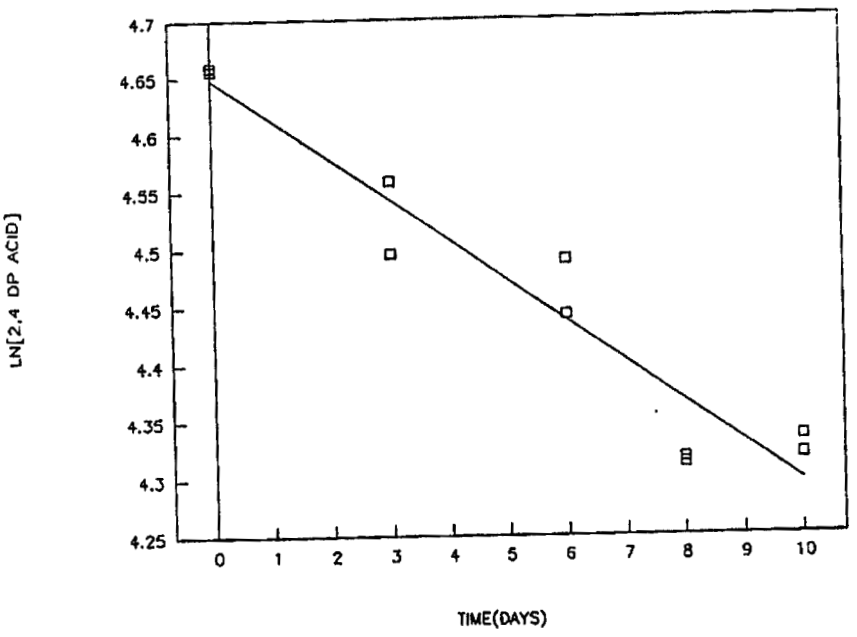


FIGURE 13. **Linear Regression Plot for Half-Life Determination Under Dark Incubation Conditions. The Half-Life Was 20 Days.**

TABLE IV. HPLC ANALYSIS OF SOIL EXTRACTS

Day	Sample	Soil Extracts[a]	2,4-DP-p acid[b]	Peak 1[b]	Peak 2[b]
Irradiated Samples					
0	LD-0-A	105.5	100.0	0.0	0.0
	LD-0-B	105.2	100.0	0.0	0.0
3	L-1-A	87.8	92.5	7.5	0.0
	L-1-B	88.8	77.5	22.5	0.0
6	L-2-A	66.4	80.0	17.2	2.8
	L-2-B	82.2	67.0	33.0	0.0
8	L-3-A	76.2	62.7	34.8	2.6
	L-3-B	61.7	64.0	33.4	2.6
10	L-4-A	65.3	73.1	24.0	2.9
	L-4-B	61.8	68.6	23.6	7.8
Dark Controls					
0	LD-0-A	105.5	100.0	0.0	0.0
	LD-0-B	105.2	100.0	0.0	0.0
3	D-1-A	96.1	99.3	0.0	0.7
	D-1-B	90.4	99.2	0.0	0.8
6	D-2-A	88.3	96.2	1.0	2.9
	D-2-B	91.1	97.8	0.0	2.2
8	D-3-A	79.6	94.1	0.0	5.9
	D-3-B	80.0	93.2	0.0	6.8
10	D-4-A	79.8	94.8	0.0	5.2
	D-A-B	80.5	94.9	0.0	5.1

[a] Percent of applied radioactivity in soil extracts. Values obtained from Table II.
[b] Percent of radioactivity detected by HPLC-RAM.

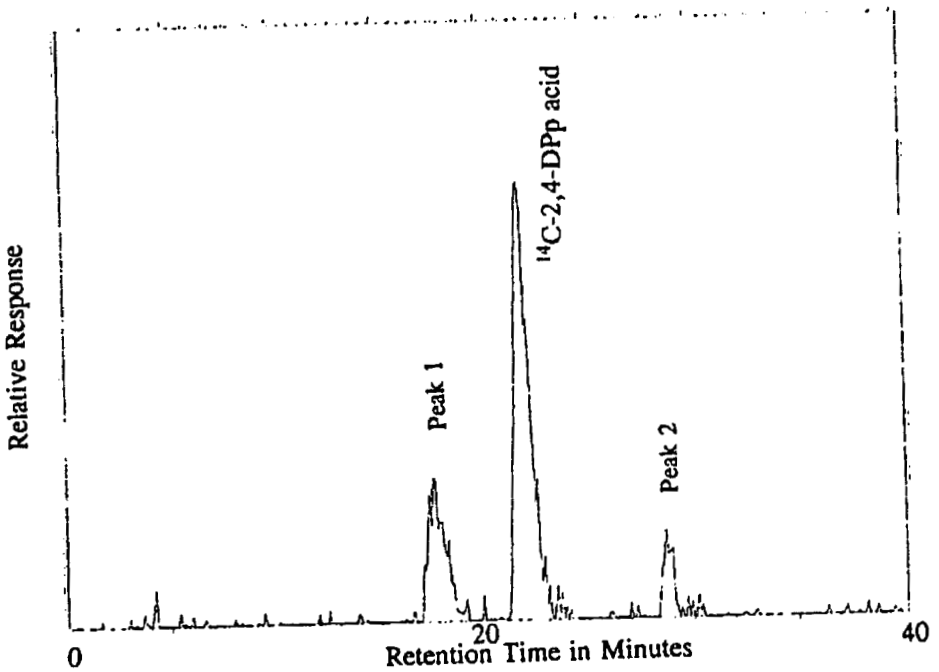


FIGURE 10. Reversed Phase HPLC Analysis of Soil Extract from Irradiated Sample L-4-B, Day 10.

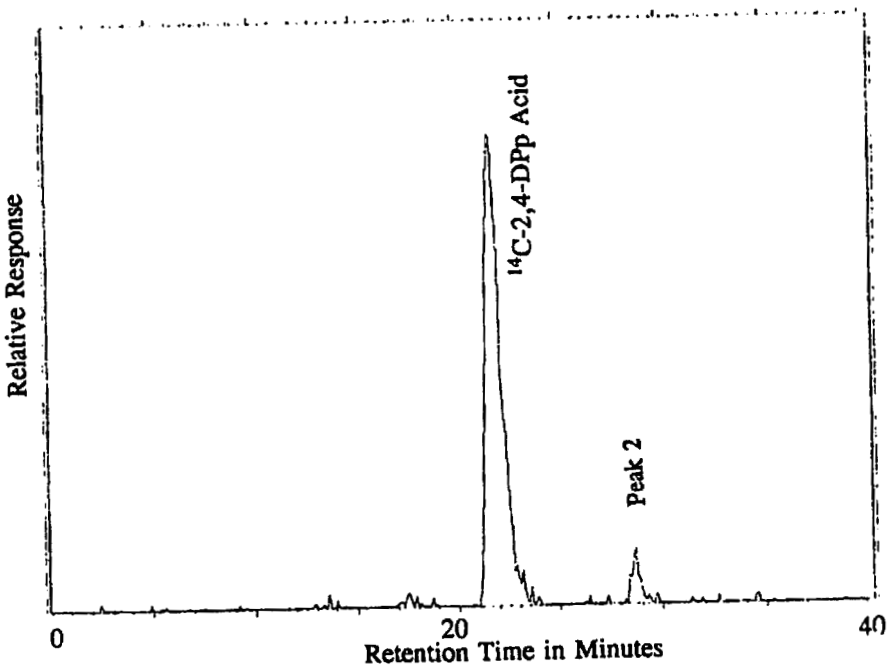


FIGURE 11. Reversed Phase HPLC Analysis of Soil Extract from Dark Control Sample D-4-B, Day 10.

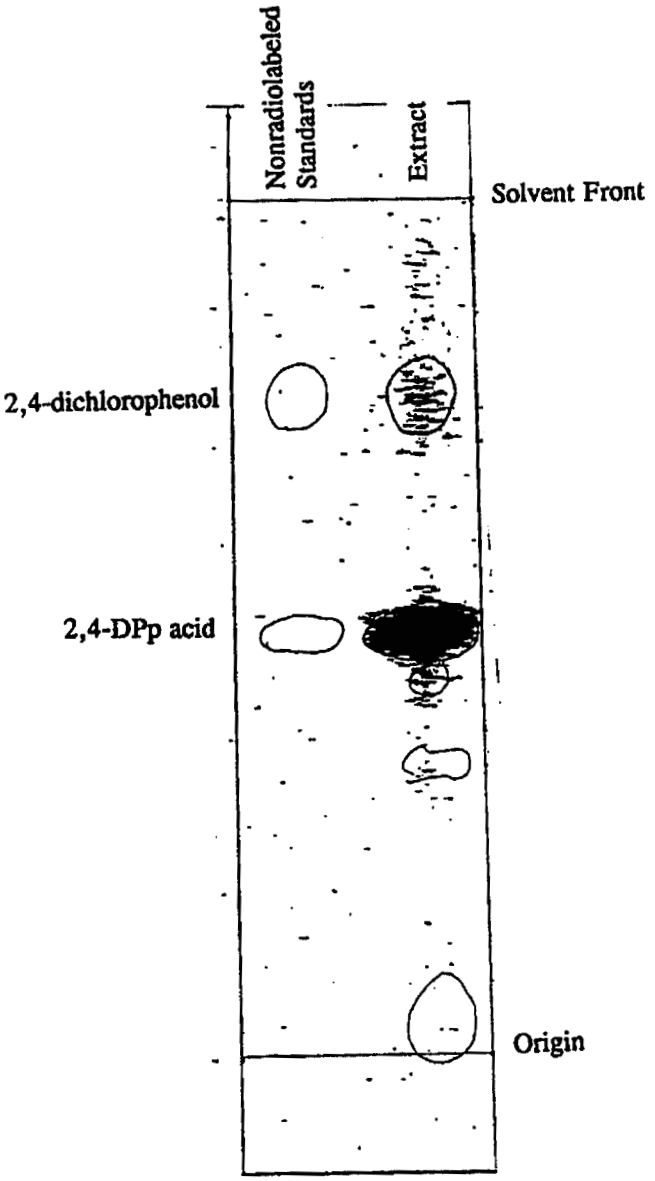


FIGURE 16. One Dimensional TLC Analysis of Concentrated Soil Extract from Irradiated Sample L-2-B, Day 6.

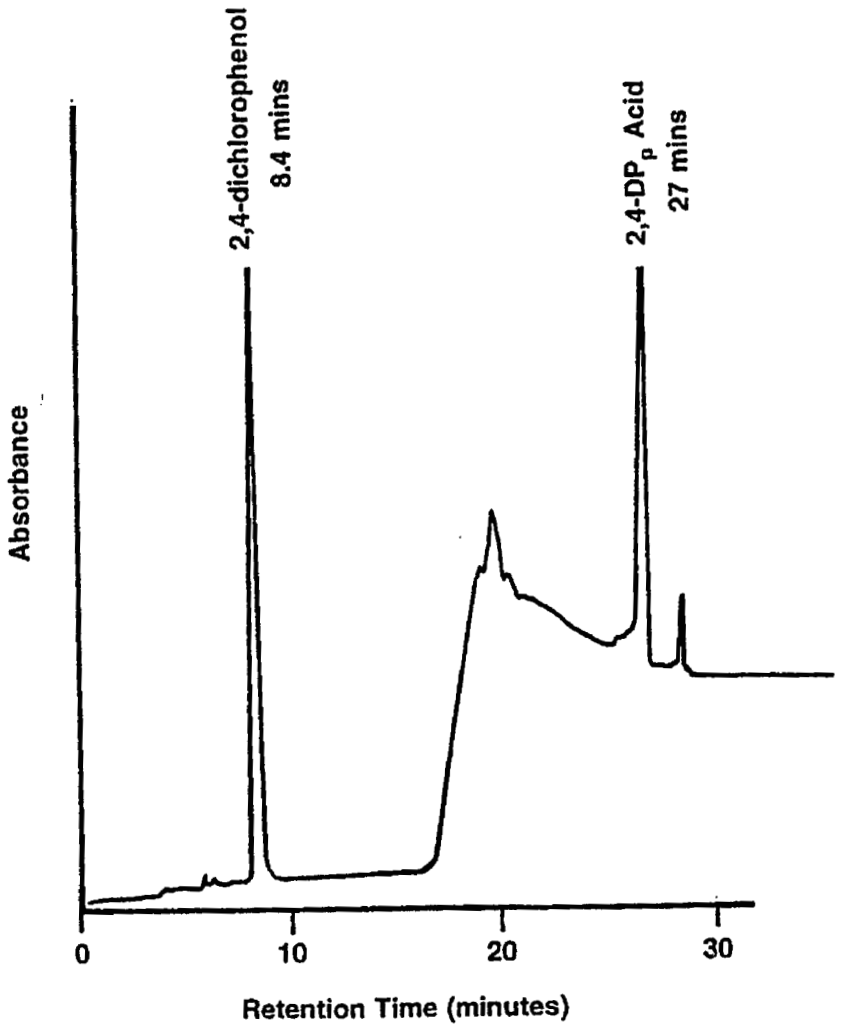
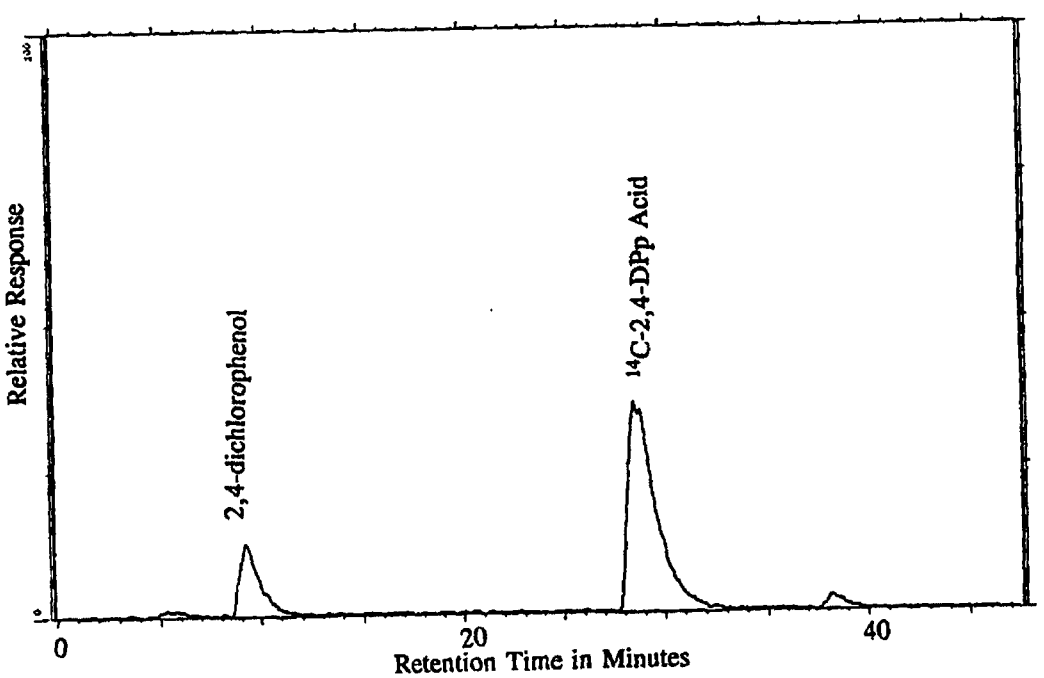


FIGURE 14. Representative UV-VIS Normal Phase HPLC Chromatogram of 2,4-DP-p Acid and 2,4-Dichlorophenol.



F GURE 15. **Normal Phase HPLC Analysis of Concentrated Soil Extract from Sample L-2-B, Day 6.**

TABLE V. DISTRIBUTION OF APPLIED RADIOACTIVITY IN ^{14}C-2,4-DP-p ACID AND DEGRADATES, INDIVIDUAL VALUES

Day	Sample	2,4-DP-p acid		Peak 1		Peak 2	
0	LD-0-A	105.5[a]	(3.38)[b]	0.0	(0.0)	0.0	(0.0)
	LD-0-B	105.2	(3.37)	0.0	(0.0)	0.0	(0.0)
3	L-1-A	81.2	(2.60)	6.6	(0.21)	0.0	(0.0)
	L-1-B	68.9	(2.20)	19.9	(0.64)	0.0	(0.0)
6	L-2-A	53.1	(1.70)	11.4	(0.37)	1.8	(0.06)
	L-2-B	55.1	(1.76)	27.1	(0.87)	0.0	(0.0)
8	L-3-A	47.8	(1.53)	26.5	(0.85)	2.0	(0.06)
	L-3-B	39.5	(1.26)	20.6	(0.66)	1.6	(0.05)
10	L-4-A	47.7	(1.53)	15.7	(0.50)	1.9	(0.06)
	L-4-B	42.4	(1.36)	14.6	(0.47)	4.8	(0.15)
Dark Controls							
0	LD-0-A	105.5	(3.38)	0.0	(0.0)	0.0	(0.0)
	LD-0-B	105.2	(3.37)	0.0	(0.0)	0.0	(0.0)
3	D-1-A	95.5	(3.05)	0.0	(0.0)	0.6	(0.02)
	D-1-B	89.7	(2.87)	0.0	(0.0)	0.7	(0.02)
6	D-2-A	84.9	(2.72)	0.9	(0.03)	2.5	(0.08)
	D-2-B	89.1	(2.85)	0.0	(0.0)	2.0	(0.06)
8	D-3-A	74.9	(2.40)	0.0	(0.0)	4.7	(0.15)
	D-3-B	74.6	(2.39)	0.0	(0.0)	5.4	(0.17)
10	D-4-A	75.7	(2.42)	0.0	(0.0)	4.1	(0.13)
	D-4-B	76.4	(2.44)	0.0	(0.0)	4.1	(0.13)

(a) Values are expressed as a percentage of radioactivity applied to sample.
(b) Values in (a) expressed as ppm. Initial application rate was 3.2 ppm.

TABLE IX. ANALYSIS OF SOIL-BOUND RESIDUES[a]

Day	Sample	Soil-bound Residues[b]	Humic Acid	Fulvic Acid	Humin	Total[c]
Irradiated Samples						
8	L-3-B	21.0	2.4	8.9	5.9	17.2
10	L-4-B	19.5	3.4	7.7	6.0	17.1

a All values as percent of radioactivity applied to soil.
b Values from Table II.
c Sum of Humic acid, Fulvic acid, and Humin